Synthesis of fused mullite and its use in multifunctional Nickel based composite coating

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Abstract:

Mullite a commonly used refractory material has been synthesized and adopted in the present study as reinforcement in the development of nickel based composite. The composite has been developed through simple electrochemical deposition method. The thermal stability of electrodeposited Ni-mullite composite in terms of microhardness was studied at temperatures upto 800^oC and compared with Ni-SiC coating, a commercially adopted wear resistant coating. The hardness value of as deposited electroforms was similar for both Ni-mullite and Ni-SiC composites (400Hk). A marginal decrease in the microhardness of Ni-mullite composite occurred at 600^oC while, significant reduction was observed beyond 400^oC for Ni-SiC coating. Thus, the Ni-mullite composite has higher thermal stability compared to Ni-SiC. The tribological studies showed that the wear volume loss for Ni-mullite composite is 2.38X10^{-5}mm^3/m while, that of Ni-SiC coating is 9.58X10^{-5}mm^3/m under identical testing conditions. The potentiodynamic polarization and electrochemical impedance studies showed that the corrosion resistance of Ni-mullite composite is better compared to Ni-SiC. Thus, it was concluded that Ni-mullite has better thermal stability, wear and corrosion resistance compared to Ni-SiC coating in other words it is a multifunctional coating.

Keywords: Fused Mullite, Ni-Mullite, Thermal Stability, Wear behaviour, Potentiodynamic polarization

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1.0 Introduction

The increasing demand from industries for improved performance, development of better surface coatings with higher wear and corrosion resistance has become imperative. Electrodeposition has the merits of simple processing and ease of fabrication, cost efficient, high productivity and good compositional control. The deposition conditions and bath chemistry can be varied so as to obtain the required properties. Nickel electroplating is utilized in large number of applications due to its advantages such as strength, toughness and resistance to corrosion/wear. Several excellent review papers concerning composite coatings have been published [1,2,3,4]. These papers focus on the uses, mechanism and models of co-deposition process. Many authors have investigated nickel-based composite coatings [5,6] in the hope of combining the corrosion resistance and strength of nickel with the hardness and oxidation resistance of some refractory compounds. Ni-SiC is one of the commercially adopted and reported wear resistant composite coating for rotary and reciprocating engines. However, its limitation is that at temperature greater than 400˚C brittle silicide formation occurs resulting in deterioration in the performance of the coating [7]. Hence, alternative reinforcements are a necessity. In the present study mullite, with a nominal composition of $3Al_2O_3$•$2SiO_2$ has been chosen as the reinforcement because of its properties like excellent high temperature properties with improved thermal shock and thermal stress owing to the low thermal expansion, good strength and interlocking grain structure. Besides its importance for conventional ceramics, mullite has become a choice of material for advanced structural and functional ceramics due to its favourable properties like low thermal conductivity, excellent creep resistance, high-temperature strength, and good chemical stability. Further, it is more homogenous in nature and has high crystal size compared to sintered mullite, hence, is predominately used at higher temperature than the sintered mullite. These interesting properties of mullite have led to the development of nickel-mullite composite coating in the present study. Also, scarce information is available on the development and properties of this coating. Radomyselskii [6] has developed composite nickel deposits by incorporating mullite whiskers into the nickel matrix and optimized the plating conditions. They studied the high temperature oxidation resistance of nickel deposits containing mullite whiskers and reported that oxidation resistance of composites is higher than that of plain nickel.

The present studies are aimed at synthesizing the particles and optimization of conditions to incorporate them mullite particles and investigates its tribological and corrosion behaviour and compare it with the most commercially used wear resistant Ni-SiC composite coating.

2.0 Materials and method

2.1 Synthesis of particles

An attempt has been made in this present work to prepare using Indian Rare Earths Limited (*IREL*), Chhatrapur produced sillimanite as raw materials in an indigenously developed thermal plasma reactor. The high temperature, good thermal conductivity and high heat content available in the thermal plasma make it ideally suitable for processing of the refractory materials. Sillimanite contains essential ingredients like Al_2O_3, SiO_2 in major concentrations for mullite preparation. Mullite from sillimanite was prepared in accordance with the following reaction:

$$\text{Sillimanite } (2Al_2O_3.2SiO_2) + \text{Alumina } (Al_2O_3) \rightarrow \text{Mullite } (3Al_2O_3.2SiO_2)$$

The compositions of the raw materials used are mentioned in Table 1. An indigenously developed 50 kW DC pot type extended arc thermal plasma reactor using graphite electrodes was used for preparation of fused mullite.

A schematic diagram of the thermal plasma reactor is shown in Fig 1. It is a pot type reactor with two graphite electrodes arranged in a vertical configuration. The graphite crucible is used as the hearth of the reactor and is connected to a graphite electrode. The whole assembly constitutes the anode. The top graphite electrode, the cathode, having an axial hole to pass plasma forming gas, is attached to a rack and pinion mechanism for vertical movement. Easily ionisable argon gas is used as plasma forming gas, which extends the arc volume considerably. The reactor is connected to a 50 kW DC thyristor controlled power source. The arc is initiated by shorting the electrodes momentarily, and pulling them apart while arc stabilization is achieved by the vertical movement of the cathode.

A typical experimental condition was: Arc current-300A, Load voltage-50 V, Charge-2 kg, Plasma forming gas Ar-1 lpm, Fusion time-10 minutes. Charge composition is Sillimanite – 60 % and Alumina – 40 %. The plasma fused product was crushed and ground to finer size for making Ni-Mullite composite coating.

2.2 Development and Characterization of Ni-Mullite composite coating

particles were characterized for its size by using particle size analyser. The average particle size of the synthesized and ground powder was 19µm. The size of the powder was further reduced by ball milling in order to obtain good mechanical properties. The particles were initially subjected to dry ball milling but, dry milling was not much effective in reducing the size. Hence, wet ball milling was carried out by using ethyl alcohol as the medium. The distribution of the size of the particle is shown in fig 2. It can be seen from the figure that the average particle size of particles after subjecting to wet milling was reduced to 4µm. These particles have been adopted in the development of the nickel composite coating. The Ni-Mullite ($3Al_2O_3$ $2SiO_2$) composite was electrodeposited from the conventional sulphamate electrolyte of composition: Ni sulphamate 550 g/l, $NiCl_2$ 6g/l , boric acid 30g/l and sodium lauryl sulphate 2ml/l. The concentration of mullite particles was varied from 25g/l - 100g/l. The particles were dispersed in the nickel electrolyte by magnetic stirring for a time period of 16 hrs prior to electrodeposition. The pH of the electrolyte was maintained at 3.0 and the electrodeposition was carried out under ambient conditions by applying a current density of $1A/dm^2$ so as to obtain a coating thickness of 50±5µm. The coating was deposited on a brass substrate as cathode of dimension 1”×1”. During the electrodeposition, particles were kept for dispersion by magnetic stirring at a speed of 400rpm.After electroplating the composite coating was cut across the cross-section using Isomet cutting machine and subsequently mounted using an epoxy resin and subjected to microhardness testing. The microhardness was tested using knoops indentor employing a load of 50gf. The readings reported are the average of five readings measured at different locations. The particle distribution across the cross-section was observed using optical microscope.

The thermal stability of the coatings was studied by subjecting the Ni-mullite composite electroforms to heat treatment at temperatures ranging from 200˚C to 800˚C for time duration of 1 hour. The thermal stability has been expressed in terms of variation in microhardness with respect to temperature. The wear resistance of the coatings was determined using pin-on-disc tribo-tester under dry sliding conditions. A hemispherical brass wear pin of 12mm diameter was coated with Ni-mullite composite and used for wear testing for a duration of 60 minutes by applying a load of 1kgf, at a speed of 200rpm, sliding distance of 2262m and a track radius of 30mm. The corrosion behaviour of the Ni-mullite coating was studied using potentiodynamic polarization and electrochemical impedance spectroscopy studies. The study was carried out in 0.25M Na_2SO_4 medium employing a three electrode system i.e the coated area ($1cm^2$) as working electrode, platinum as counter electrode and standard calomel electrode as reference electrode. The corrosion studies were performed using CH instruments (CHI6042D) Electrochemical workstation. The working electrode was immersed in Na_2SO_4 solution for an hour in order to stabilize the open circuit potential (E_{ocp}). EIS studies were carried out in the frequency range 100kHz to 10mHz. The impedance data is displayed as Nyquist and Bode plots. The Nyquist plot obtained is a plot of real (z′) Vs imaginary (Z″) and Bode plot is a plot of |Z| Vs Frequency and phase angle (θ) Vs frequency, where |Z| is the absolute impedance. The potentiodynamic polarization measurements were carried out with upper and lower potential limits of ±200mV with respect to E_{ocp}. The tafel plot obtained is represented as potential vs log i.

The coating was characterized for its surface morphology using field emission scanning electron microscope (FESEM) and the composition by energy dispersive X-ray analysis, EDAX. The X-ray diffraction studies were done to determine the crystallite size and crystal structure. The crystallite size was determined using Scherrer equation [8] $D= k\lambda/(\beta\cos\theta)$ where, k is the scherrer factor ≈1, D the crystallite size, λ the incident radiation wavelength, β the integral breadth of the structurally broadened profile, θ the angular position.

3.0 Results and discussion

3.1 Electrodeposition of Ni-Mullite composite

Ni-mullite composite coatings were obtained at different mullite particle concentrations of 25g/l, 50g/l, 75g/l and 100g/l. The effect of particle concentration on the microhardness is seen in fig 3. From the graph the average microhardness values obtained for the four Ni-Mullite composite coatings are 339Hk, 405Hk, 403Hk, 402Hk respectively. The particle content was optimized as 50g/l as the maximum microhardness is displayed at this concentration. Thus, it is seen that the reinforcement of fused mullite particles in nickel matrix improved its microhardness (280Hk). I.D Radomyselskii optimized the electrolyte pH to 2-3, working current density 4-5 A/dm^2 and temperature 25-30^{0}C for mullite whisker reinforced Ni matrix composite. They reported that current density variation from 1 to 5A/dm^2 has no significant effect on particle deposition. Raising the deposition temperature to 60^{0}C led to pit formation which could not readily be prevented by addition of various surface active agents[6].

3.2 Thermal stability Studies

Thermal stability of the coatings has been studied in terms of microhardness. The influence of temperature on the microhardness is shown in fig 4. It can be observed from the graph, that the microhardness of the as deposited coating is 405Hk, which increased to 435Hk when it was heated to 200˚C for one hour. Increase in temperature from 200^{o}C to 400˚C resulted in a significant decrease in the microhardness (368Hk). Beyond 400˚C a marginal decrease in the microhardness is observed. Beyond 600˚C a significant reduction in the microhardness is observed (168Hk). The microhardness value has also been correlated with the size of the indentation. The cross-sectional optical micrographs of as plated and heat treated Ni-Mullite electroforms are shown in fig.5. It can be inferred from the images that the size of the indentation is small for 200˚C heat treated electroform and this can be associated with its marginally high microhardness compared to as deposited electroform. The microhardness value decreased for 400˚C heat treated electroform hence, an increase in the size of the indentation is observed. An increase in temperature from 400^{o}C to 600˚C, resulted in an insignificant difference in the microhardness which can be correlated with the similar size of the indentation impressions on the electroforms. Beyond 800˚C a significant reduction in the microhardness value is seen and this can be associated with the big size of the indentation impression. The microhardness values of heat treated Ni-Mullite and Ni-SiC composite coatings is tabulated in Table 2 and shown in Fig.4. It can be seen from the figure that the microhardness of nickel improves significantly upon reinforcing with ceramic particles like fused mullite and SiC. Further, it is seen that the microhardness values are almost similar upto 400˚C for both Ni-mullite and Ni-SiC coatings. However, beyond 400˚C there is a gradual reduction in the microhardness of Ni-SiC coating. This shows that Ni-SiC is thermally stable upto 400^{o}C whereas the developed Ni-Mullite composite coating is thermally stable upto 600^{o}C. Thus, the incorporation of fused mullite particles in nickel matrix enhances the thermal stability of nickel to 600^{o}C, which is better than reinforcing nickel with silicon carbide particles.

3.3 Characterization

The surface morphology of as deposited Ni-Mullite, Ni-SiC and heat treated Ni-Mullite composite coatings are depicted in the figures 6 and 7. Ni-Mullite coating displays big nodular morphology with fused mullite particles distributed throughout whereas the Ni-SiC coating, displays small nodular morphology wherein the SiC particles are not distinctly visible on the surface. In other words, SiC particles are covered by a film of nickel. The 400˚C heat treated Ni-mullite coating shows a reduction in the nodularity, but no change in the matrix morphology is noticed. A featureless surface with black particles distributed throughout the surface is seen for 800˚C heat treated Ni-mullite composite coating. The localized EDX analysis confirmed the black particles as mullite.

The X-ray diffractograms of Ni-Mullite composite coatings are shown in fig.8. XRD analysis revealed that the predominant reflection exhibited by as deposited and 400˚C heat treated Ni-mullite coatings corresponds to Ni (200) along with Ni (111) reflections. The 800˚C heat treated coating displayed the presence of NiO along with nickel reflections (200) and (111). Grain size was calculated for as deposited, 400˚C and 800˚C heat treated composites with respect to (200) reflection. The crystallite sizes are 38nm, 27nm and 73nm respectively. A decrease in the grain size is seen for 400^{o}C heat treated coating compared to the as-deposited coating which correlates with its higher microhardness. A significant increase in the grain size is observed for 800^{o}C heat treated composite correlating with its low microhardness i.e grain softening. Thus, the relation between grain size and microhardness follows the Hall- Petch relationship, which states that hardness is inversely proportional to crystallite size.

3.4 Tribological behaviour

The tribological behavior of the coatings was evaluated under dry sliding conditions. The wear loss values for both Ni-mullite and Ni-SiC composites are listed in table 3. From the table, it is observed that the wear volume loss of Ni-mullite composite coating is less compared to Ni-SiC composite coating showing its better wear resistance. Also, the wear is burnishing wear (10^{-6}) for Ni-SiC. The wear is intermittent between moderate and burnishing wear for Ni-mullite composite coating. Thus, it can be inferred from the above studies that the incorporation of mullite particles in nickel matrix resulted in a coating with enhanced mechanical properties like microhardness and wear resistance compared to Ni-SiC. Fig 9 shows the microtopographic image of the wear track on the disc tested against the coated pin. No loss of material from the disc is observed during the wear testing of Ni-mullite composite coating, thereby confirming that the material loss has occurred exclusively from the coating.

3.5 Corrosion behaviour

3.51 Potentiodynamic polarization studies

Initially the system was allowed to attain open circuit potential for 3600 sec. After the stabilization of open circuit potential, the upper and lower potential limits were fixed to ±200mv w.r.t E_{ocp} for carrying out the potentiodynamic polarization studies. The sweep rate applied was ±100mv/s. Fig. 10 indicates the polarization curves of mild steel substrate coated with nickel-mullite subjected to corrosive medium, 0.25M Na_2SO_4 solution. The electrochemical parameters such as corrosion potential, E_{corr} corrosion current density i_{corr} and polarization resistance, R_p are listed in table 4. In principle, a high corrosion potential and low corrosion current density has better corrosion resistance. Stern-Geary [9] equation was employed to determine the corrosion current density. The polarization resistance was calculated using the equation, $R_p = (E/I)/E \rightarrow 0$ where E is the polarization potential, I is the polarization current. Tafel plot was displayed and E_{corr}, i_{corr} were deduced from the plot. From the plot the corrosion current density obtained for Ni-Mullite is 3.09μA/cm^2, for Ni- SiC it is 7.07μA/cm^2. The corrosion potential for Ni-mullite is -0.4019 V/dec and for Ni-SiC it is -0.46 V/dec. Ni-mullite is showing slight positive shift in the potential and also its corrosion current density is less compared to Ni-SiC. The polarization resistance is also high for Ni-mullite composite coating indicating beter corrossion resistance of Ni-mullite compared to Ni-SiC composite coating.

3.52 Electrochemical impedance studies

Electrochemical impedance spectroscopy enables to obtain the information about corrosion reaction mechanism of the system. Nyquist and Bode plots for coated samples immersed for 1 hour in 0.25M Na_2SO_4 solution are shown in figs 11 and 12. The Nyquist plot of Ni-SiC is showing single semicircle, which is slightly flattened for Ni-mullite and this is a characteristic of two time constants. Electrochemical impedance data obtained by equivalent circuit fitting for Ni-mullite composite coating and Ni-SiC are shown in table 5. The acquired data was curve fitted. For Ni-mullite coating two time constant was obtained with R(QR)(QR) as equivalent circuit which indicates two reactions, the first reaction is expected to be the reaction between the electrolyte and the interface between the nickel matrix and the particles and the second reaction is the reaction between the electrolyte and the nickel matrix. The single time constant obtained for Ni-SiC with equivalent circuit R(QR) indicates single reaction which is uniform corrosion occurring on the surface of the coating. Although, two reactions are taking place in Ni-mullite coating the overall corrosion rate is less which can be seen from its high Rct value, indicating better corrosion resistance compared to Ni-SiC composite coating.

4.0 Conclusions

Fused mullite particles were synthesized from sillimanite in a thermal plasma reactor. The synthesized particles were reinforced in nickel matrix by electrodeposition method. The developed Ni-mullite composite coating was characterized and evaluated for its mechanical and chemical properties. A maximum microhardness of 405Hk was observed for a particle content of 50g/l in the electrolyte. The incorporation of fused mullite particles improved the thermal stability of nickel from 400^{o}C to 600^{o}C and the thermal stability of Ni-mullite coating was better (600^{o}C) compared to Ni-SiC (400^{o}C) coating. The tribology testing showed an improvement in the wear resistance of nickel upon reinforcement of fused mullite particles, further its wear resistance was better compared to Ni-SiC coating. The potentiodynamic polarization and electrochemical impedance studies revealed better corrosion resistance behavior of nickel reinforced fused mullite composite coating compared to Ni-SiC coating.

Thus, nickel-mullite coating can be used as a thermally stable, wear resistant and corrosion resistant coating, in other words it is a multifunctional coating and an alternate to Ni-SiC coating, the most commercially used wear resistant coating.

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Table 1. Compositions of raw materials

Sillimanite	Wt %
Al_2O_3	58.0
SiO_2	38.1
Fe_2O_3	0.37
TiO_2	0.33

Alumina	Wt %
Al_2O_3	99.8
SiO_2	0.01
Fe_2O_3	0.01
Na_2O	0.10

Table 2. Comparative microhardness values of Ni- SiC and Ni-Mullite

Coating	As deposited, Hk_{50gf}	200^oC, Hk_{50gf}	400^oC, Hk_{50gf}	600^oC, Hk_{50gf}	800^oC, Hk_{50gf}
Ni-SiC	407	391	372	200	120
Ni-Mullite	404	435	368	335	168

Table 3. Comparative wear results for plain Nickel, Ni- SiC and Ni-Mullite

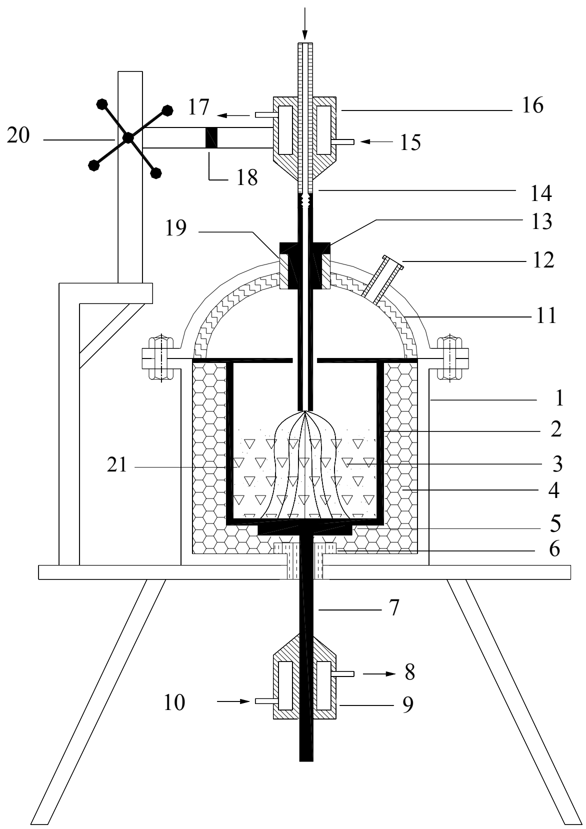
Coating	Wear volume loss mm^3/m
Ni-SiC	$9.58X10^{-5}$
Ni-Mullite	$2.38X10^{-5}$

Table 4. Potentiodynamic polarization data for Ni-Mullite cmposite coating.

Coating	I corr $\mu A/cm^2$	Ecorr V/dec	Rp K ohm cm^2
Ni-Mullite	3.09	-0.40	10123
Ni-SiC	7.07	-0.46	5012

Table 5. Electrochemical impedance data for Ni-Mullite and Ni-SiC composite coatings

Sample	Rs K ohm cm^2	Q_{film}	n_{film}	R_{fim} K ohm cm^2	Q_{dl}	n_{dl}	R_{ct} K ohm cm^2
Ni-mullite	1.34	$9.11X10^{-5}$	0.92	1793	$2.48X10^{-4}$	0.90	7137
Ni-SiC	2.73	-	-	-	$1.35X10^{-4}$	0.90	4301



1. M.S. casing, 2. Graphite crucible, 3. Plasma, 4. Bubble alumina, 5. Graphite base, 6. Alumina bush, 7. Bottom electrode (graphite), 8. Water outlet, 9. Copper connector, 10. Water inlet, 11. Magnesialining, 12. Exhaust, 13. Graphite bush, 14. Top electrode (graphite), 15. Water inlet, 16. Copper connector, 17. Water outlet, 18.Electrical insulation, 19. Alumina bush, 20. Rack and pinion arrangement and 21. Charge

Fig. 1: Schematic diagram of the indigenously developed extended arc plasma reactor

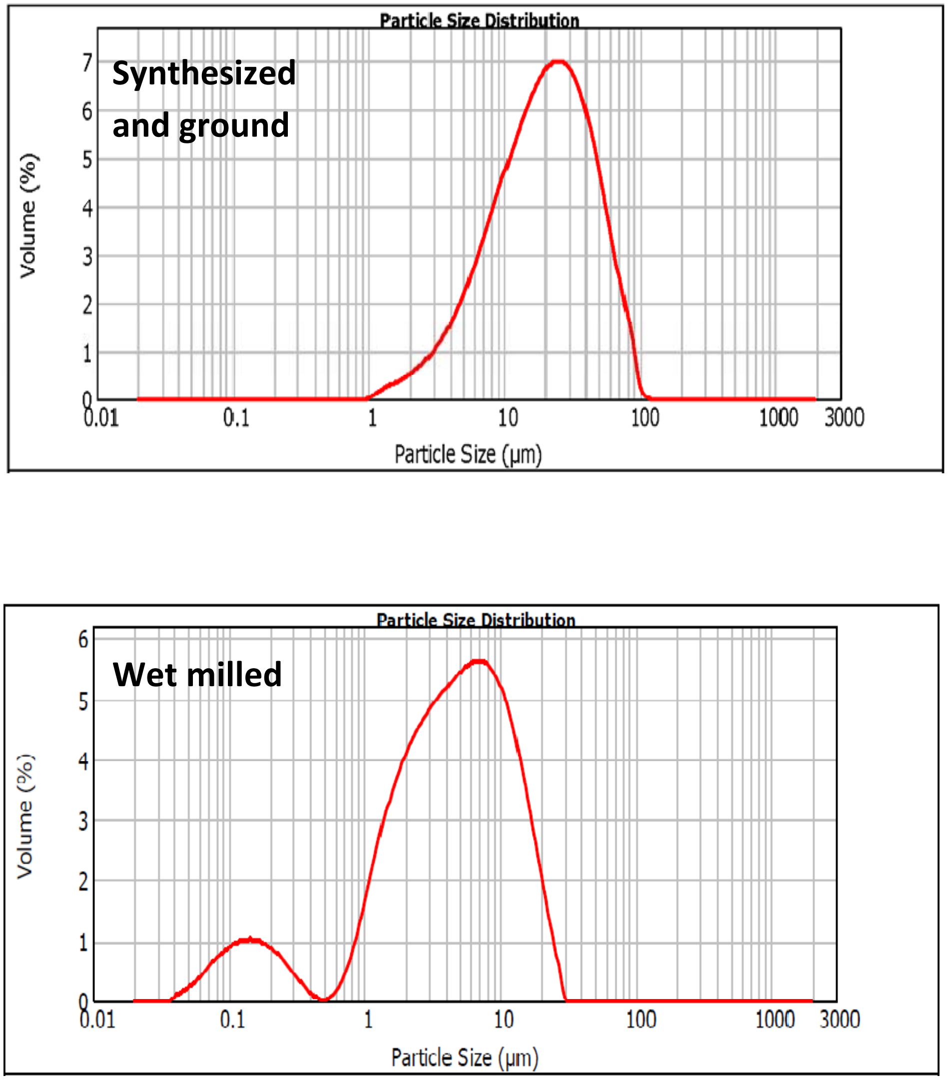


Fig.2: Particle size analysis result of as received and wet milled Mullite powder

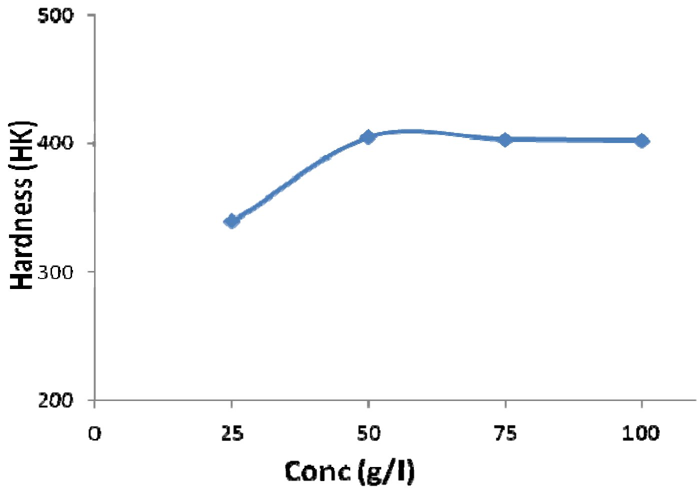


Fig.3: Effect of particle concentration on the microhardness of Ni-Mullite coating

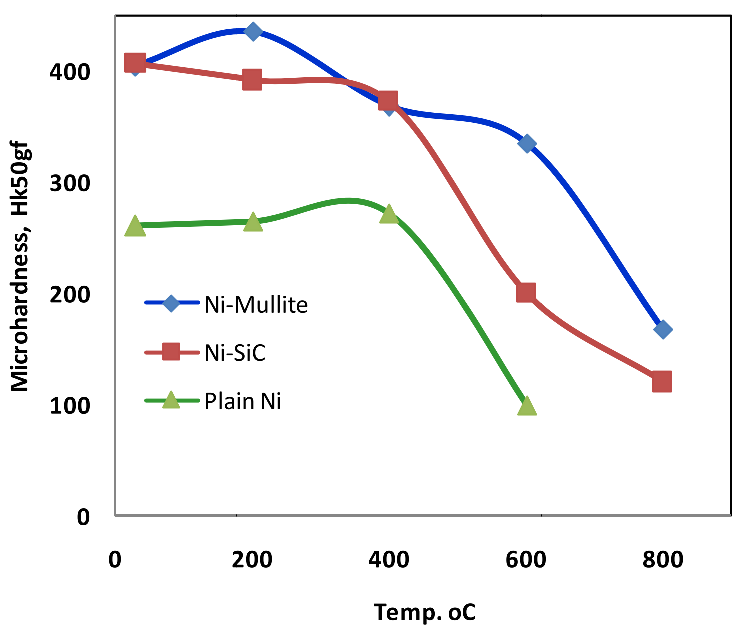


Fig.4:Influence of temperature on the microhardness of Ni-Mullite, Ni-SiC and plain Ni coatings

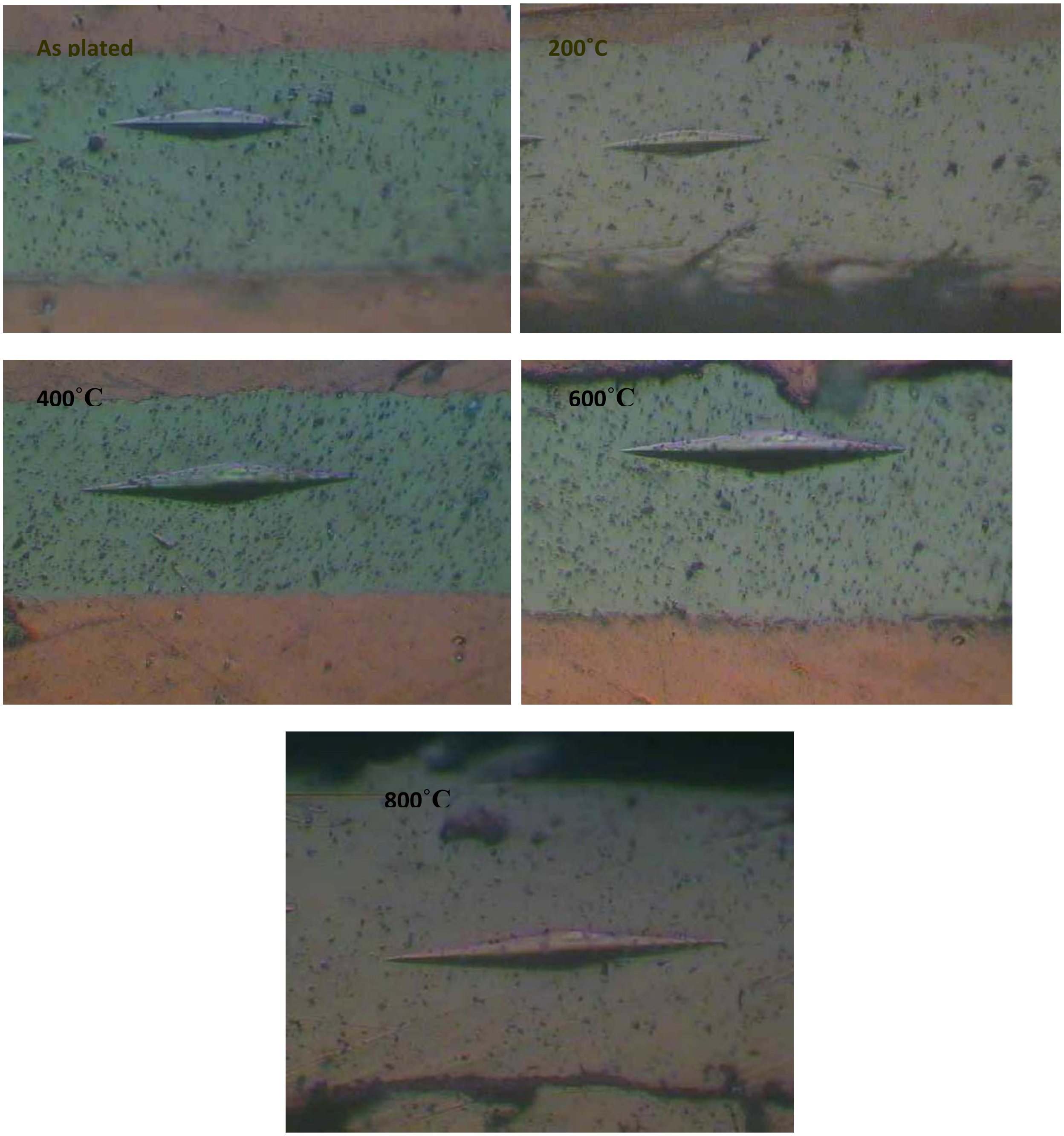
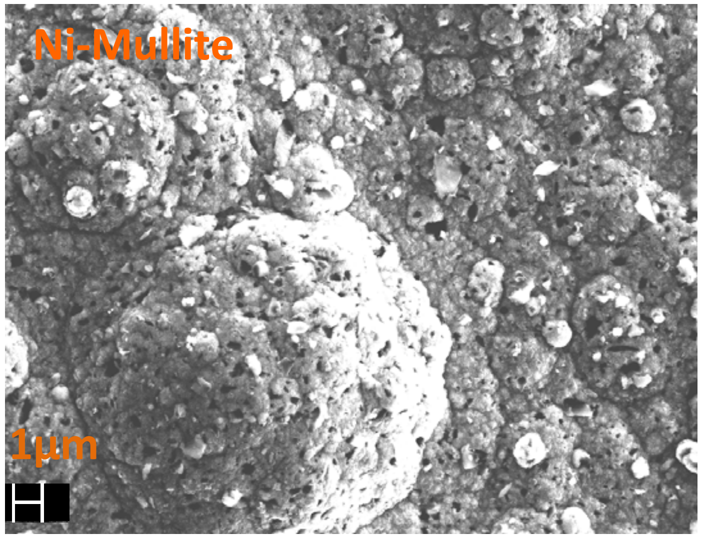


Fig. 5: Cross sectional image of as plated, 200˚C, 400˚C, 600˚C and 800˚C heat treated Ni-Mullite coating



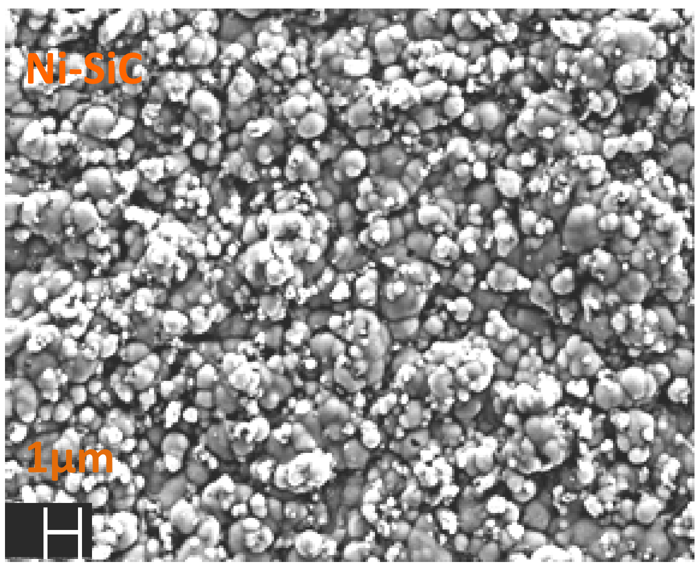


Fig. 6:.Surface morphologies of as plated Ni-Mullite and Ni-SiC composites

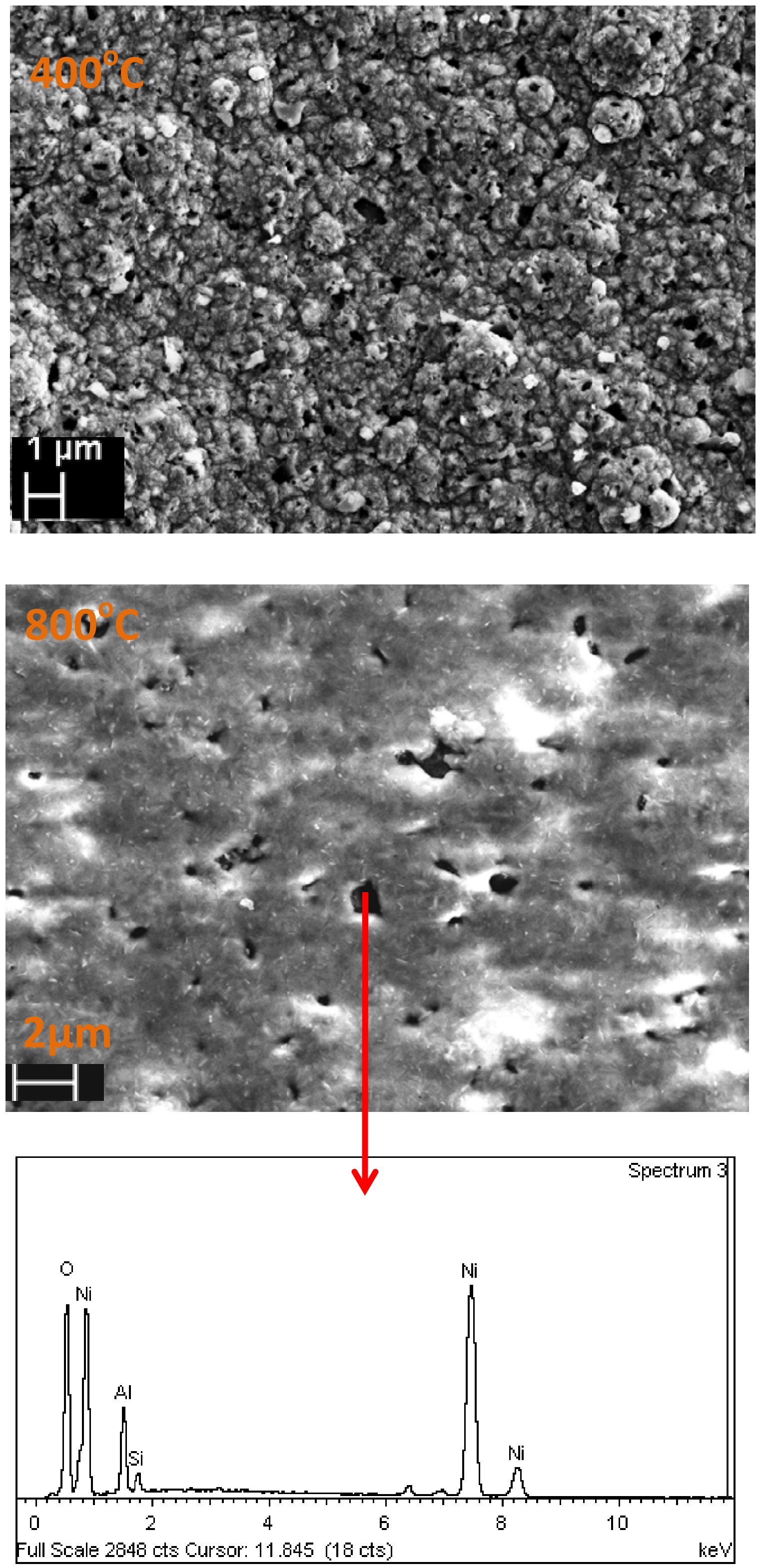


Fig.7: Surface morphologies of 400°C heat treated and 800°C heat treated Ni-Mullite coating

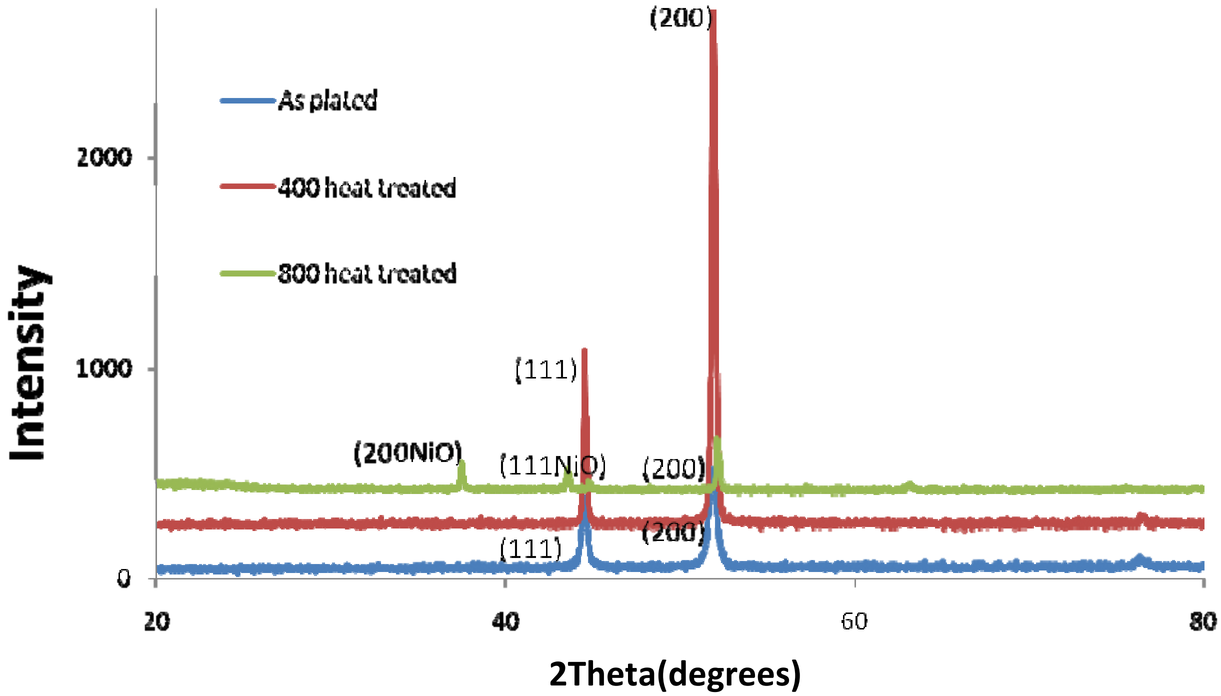


Fig. 8: X-ray Diffractograms of as plated, 400˚C and 800˚C heat treated Ni-Mullite coating

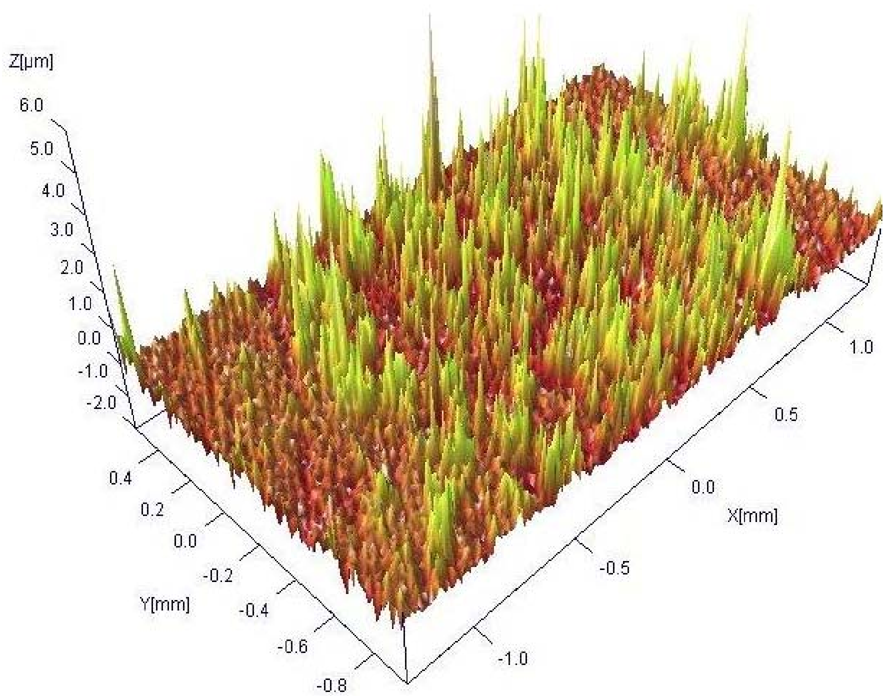


Fig. 9: Microtopographic image of Wear track on the hardened Cr steel disc tested against a Ni-Mullite coated pin

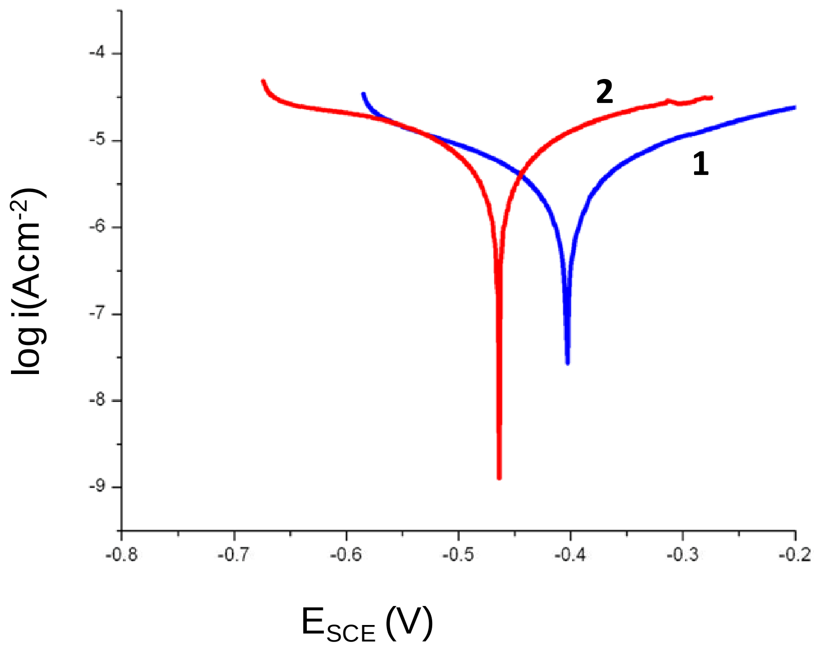


Fig. 10: Potentiodynamic polarization curves for Ni-Mullite (1) and Ni-SiC (2) coatings

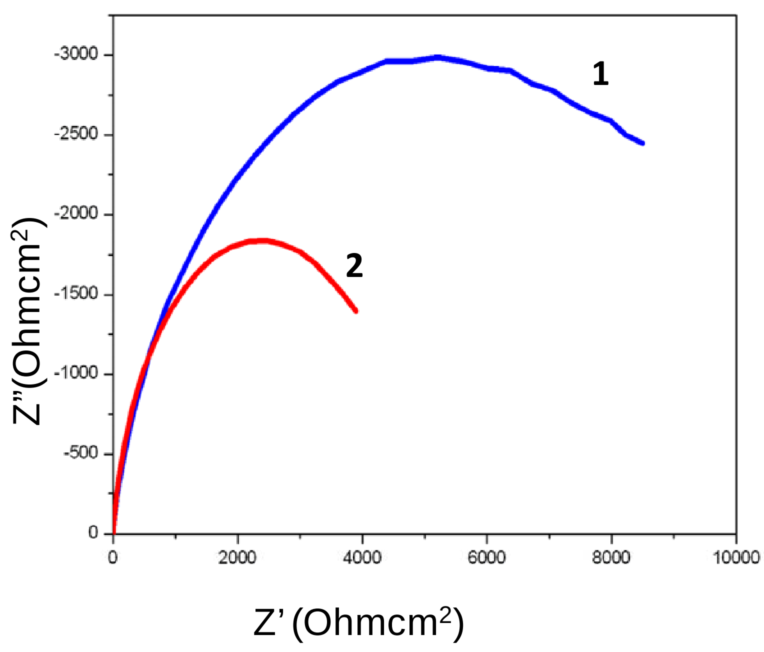


Fig.11: Nyquist plot for Ni- Mullite (1) and Ni- SiC (2) coatings

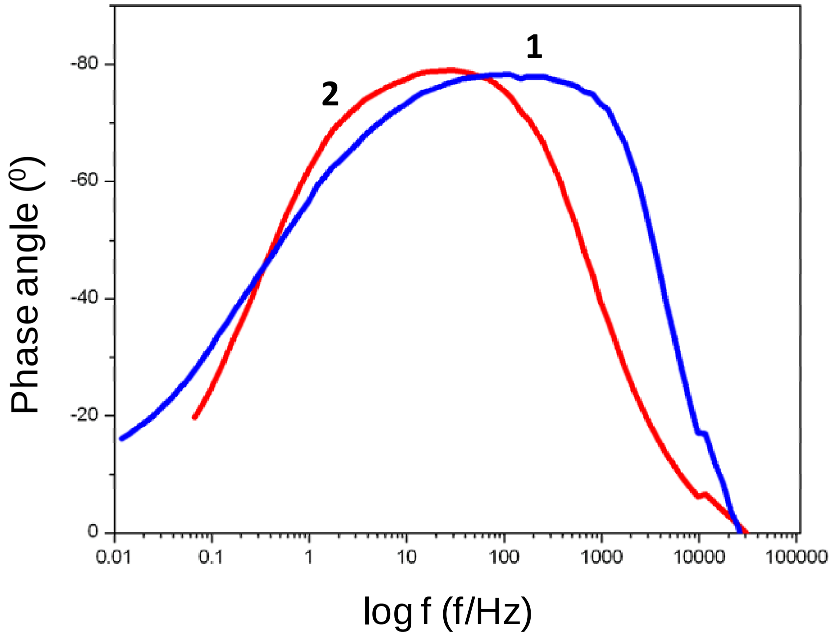


Fig.12: Bode plot for Ni- Mullite (1) and Ni-SiC (2) coatings